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(54) **Whisker-reinforced ceramic body.**

(57) According to the present invention there is now provided a whisker reinforced ceramic body comprising 2-50 % by volume whiskers and/or fibers and/or platelets and/or submicron particles in a ceramic matrix manufactured by powder metallurgical methods, i.e., dispersion in a suitable liquid, granulation, compaction and sintering. If the granulation is performed by freeze granulation a ceramic body with homogeneous structure with essentially no granule borders is obtained.

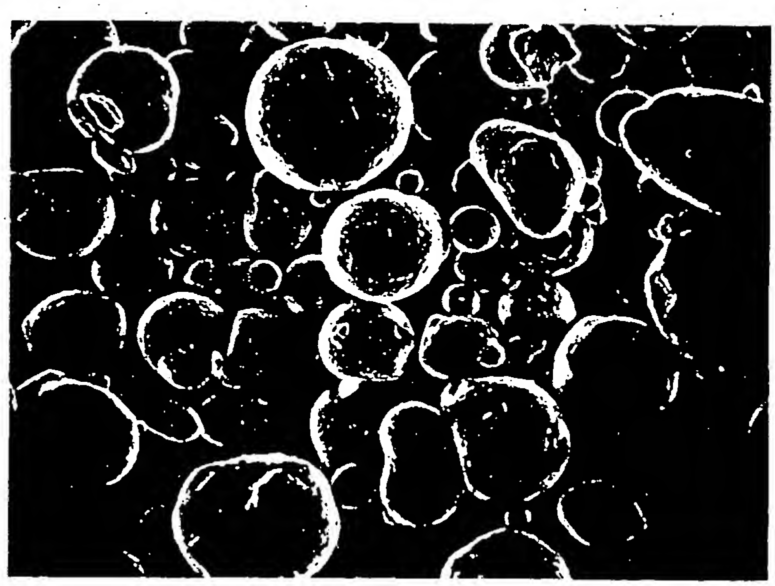

Fig. 4

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The present invention relates to whisker reinforced ceramic bodies in particular ceramic cutting tool inserts with improved structure homogeneity.

It is well known in the art that the fracture toughness of a ceramic material can be increased by addition of mono-crystalline hair crystals (whiskers) and/or platelets. SiC-whiskers in an alumina matrix are disclosed in US 4,543,345. US 4,867,761 discloses the use of carbides, nitrides or borides of Ti and/or Zr in an alumina matrix. US 4,849,381 discloses a cutting tool insert comprising a mixture of whiskers and platelets.

Cutting tool inserts made of SiC-whisker-reinforced alumina are an established product on the cutting tool market mainly for machining of heat resistant materials and to some extent for machining of cast iron.

Whisker reinforced ceramic inserts are generally manufactured by uniaxial pressure sintering. Another possible way to manufacture such inserts is by tool pressing and glass encapsulated hot isostatic pressing. This latter manufacturing way is mainly used for inserts with more complex geometries. In both cases the powder that is filled into the pressing tool has to be granulated in order to obtain necessary flow properties. The most common way of granulating such powders is by spray-drying technique. Spray drying means that a slurry containing the powdery components of the final composition is dried and granulated in hot gas in the same process step. However, during spray drying the whiskers are drawn into the middle of the granules and the granule borders are depleted of whiskers. As a result the granules have a core armoured by whiskers and for that reason cannot be completely crushed during the subsequent compaction process. This leads to an inhomogeneous structure with visible granule borders in the sintered material.

GB 2214178 discloses the manufacture of whisker reinforced ceramics by freeze drying the whisker/powder suspension. The resulting 'cake' is then shaken to break up the agglomerates and sifted through a 1 mm sieve. The powder is then compacted and sintered. The powder obtained after sifting has very poor flow properties and the method can only be used in the manufacture of bodies of simple shape such as cylinders, circular discs etc which are subsequently ground to final shape and dimension. Although GB 2214178 claims that the resulting material showed the whiskers to be well-dispersed, a certain segregation can not be avoided during the freezing at least on a larger(commercial) scale and as a result the sintered body has inhomogeneous whisker distribution.

A method of obtaining a whisker reinforced ceramic body with a structure essentially free of granule borders and an essentially one-dimensional whisker orientation by injection molding is disclosed in Swedish patent application 9100895-3.

In Swedish patent application 9201376-2 a method of forming ceramic bodies by temperature induced flocculation is disclosed which, if applied to whisker reinforced ceramic bodies, gives a structure essentially free of granule borders and with an isotropic whisker orientation.

According to the present invention it has been found that if drying and granulation are performed by freeze granulation it is possible to manufacture whisker reinforced ceramics with an improved homogeneity of the structure.

Fig 1 is a light optical micrograph in 100X of a cross section parallel to the pressing direction of a ceramic material consisting of Al_2O_3 reinforced with SiC-whiskers manufactured by spray drying and uniaxial pressure sintering as known in the art.

Fig 2 is a corresponding micrograph of a material manufactured by freeze granulation according to the present invention.

Fig 3 is a scanning electron optical micrograph in 50X of a granulated powder according to prior art, GB 2214178.

Fig 4 is a scanning electron optical micrograph in 50X of a granulated powder according to the present invention.

According to the present invention there is now provided a whisker reinforced ceramic body manufactured by powder metallurgical methods, i.e., dispersion in a suitable liquid, granulation, compaction and sintering. By using a granulated powder having essentially spherical granules with a homogeneous distribution of whiskers and therefore readily crushed during the subsequent compaction, ceramic bodies are obtained having a homogeneous structure and composition with essentially no granule borders and, in the case of a uniaxial compaction, an essentially two-dimensional whisker-orientation.

The degree of orientation (texture) of the whiskers of a uniaxially compacted whisker-reinforced body can be determined by X-ray diffraction, A texture coefficient, T, can be defined which in the case of a SiC-whisker-reinforced body, where the SiC-phase is present as >95% β-SiC-whiskers, reads as follows:

$$T = [(SiC_1/SiC_2)_p/(SiC_1/SiC_2)_c]^{0.5}$$

where SiC_1 = the intensity from the $\{10\bar{1}0\}$-peak of the hexagonal α-SiC

SiC_2 = the sum of the intensity from the {111}-peak of the cubic β-SiC and {0002} peak of the hexagonal α-SiC

p is from a plane perpendicular to the direction of the compaction

c is from a plane parallel to the direction of the compaction

For a ceramic body according to the invention T>3 preferably >4, most preferably >5.

Bodies according to the invention are made by thoroughly mixing ceramic powders preferably by dispersion in water or an organic solvent with suitable freezing point. The dispersion can be facilitated/improved by addition of organic additives and/or by adjustment of the pH-value when dispersing in water. If the powder shall be tool pressed, binders are added. The dry content of the dispersion shall be in the range 10-50 % by volume, preferably 25-40% by volume. The dispersion is sprayed into a vessel having a temperature well below the freezing point of the dispersing medium, preferably into a vessel containing liquid nitrogen. The frozen granules are then transferred into a freeze drier where the frozen liquid is sublimated at suitable subpressure and temperature. After freeze-drying a powder is obtained with good flow properties which then is compacted to bodies of desired shape and sintered in accordance with known technique. The compaction is made by uniaxial pressure sintering, by tool pressing or isostatic pressing. In the two latter cases glass encapsulated hot isostatic pressing follows.

The granules of the granulated powder are spherical of essentially the same relative density as the dispersion and with a uniform distribution of whiskers and/or platelets. The diameter of the granules is in the range 0.01-1.0 mm, preferably 0.05-0.5 mm, generally with a low spread in size, fig 4. Good flow properties are necessary when using uniaxial pressure sintering to get an even filling of the die to ensure even density in the sintered disc. In case of tool pressing good flow properties are necessary when manufacturing ceramic bodies of complex shape such as cutting tool inserts with complex chip breakers i.e. comprising a plurality of projections and recessed areas. In this latter case the bodies are given their final shape in the pressing operation with essentially no grinding being necessary after the sintering.

Granulated powders and bodies according to the invention comprise all kinds of whisker reinforced ceramic materials comprising, in addition to conventional sintering aids and/or grain growth inhibitors, 2-50, preferably 15-35 % by volume of single crystals whiskers and/or fibers and/or platelets and/or submicron particles of carbides, nitrides and/or borides of Si, Ti, Zr, Hf, Ta, and/or Nb or solid solutions thereof. The whisker/fiber material consists of hair-shaped monocrystals/polycrystals with a diameter of 0.2-10 μm and a length of 2.5-100 μm and a length/diameter ratio of preferably 5-10. The platelets are monocrystal plates with a diameter of 0.5-40 μm and a diameter/thickness ratio of 5-50, preferably 10-20. The submicron particles generally have a size <500 nm.

The grain size of the ceramic matrix shall be <10 μm, preferably <4 μm. The matrix is based on ceramic oxides, preferably Al_2O_3, or ceramic nitrides, preferably Si_3N_4, possibly further containing hard carbides and/or nitrides and/or borides and/or binder metal. The ceramic matrix shall preferably contain <20 volume-% ZrO_2. The relative density shall be at least 95 %, preferably 98 %, most preferably 99 %.

Example 1

A ceramic slurry was manufactured in a conventional way by wet dispersion in water. The dry content was 28% by volume of ceramics with the composition 75 weight-% alumina with sintering aid and 25 weight-% SiC-whiskers. The slurry was then divided into two parts. One part was dried and granulated by conventional spray-drying technique. The other part was sprayed into a vessel containing liquid nitrogen and afterwards freeze dried at a temperature of about -20°C.

Both powders were then uniaxially pressure sintered at a pressure of 30 MPa and a temperature of 1850°C for 1 hour to round discs with the diameter 80 mm and the height 5.5 mm. From the discs square inserts with the style SNGN 120408 T02520 were manufactured.

The microstructure of the inserts made from freeze granulated powder, fig. 2, shows a more homogeneous distribution of SiC-whiskers compared to the insert made from spray-dried powder, fig. 1, in which the original whisker depleted granule borders appear as a network surrounding the whisker-enriched original granule cores. The granules have been somewhat compressed in the pressing direction. The t-value was for the insert according to prior art 2.81 and for the insert according to the invention 4.54.

Example 2

The inserts from example 1 were tested in a longitudinal turning operation according to the following:

Workpiece: Inconel 718Å
Cutting speed: 150 m/min
Cutting depth: 2.0 mm
Feed: 0.1 mm/rev

Result (time to notch wear >2 mm in minutes (mean of three tests))	
Variant A (prior art)	4.5
Variant B (according to the invention)	6.0

These results indicate that the more favourable whisker distribution of variant B has resulted in a reduced notch wear.

Example 3

A ceramic slurry was manufactured in the same way and with the same composition as in the case of example 1 with the addition of polyvinylalcohol and glycerol to the slurry. The slurry was divided into two parts. One part was dried and granulated by conventional spray-drying technique. The other part was sprayed into a vessel containing liquid nitrogen and afterwards freeze dried at a temperature of about -20°C.

Both powders were manufactured in a so called Q-cut™ geometry by tool pressing. This geometry consists of an insert and a holder. The compacted bodies were treated in a combined debinding and presintering cycle in a graphite furnace. The final temperature was 1300°C and the furnace atmosphere was hydrogen. The presintered bodies were dipped with a suction cup in a BN-slurry and then in a mullite slurry according to Swedish patent application 9004134-4. The bodies, which now were surrounded by a covering BN-layer and on top of this a covering mullite layer, were placed in a glass powder bed and after that sintered by isostatic pressing at high temperature. Before the isostatic pressing the glass was melted in order to isolate the bodies from the overpressure in the furnace. The sintering was performed at 1550°C and 160 MPa. The microstructure of the bodies made from freeze granulated powder showed an obvious more homogeneous distribution of SiC-whiskers compared to the bodies made from spray-dried powder.

Example 4

The bodies from the preceding example were ground peripherally to a diameter of 6.35 mm and edge-treated and afterwards tested in a longitudinal turning operation according to the following:

Workpiece: Inconel 718Å
Cutting speed: 200 m/min
Cutting depth: 1 mm
Feed: 0.15 mm/rev

Result (time to notch wear >2 mm in minutes (mean of three tests))	
Variant A (prior art)	5.0
Variant B (according to the invention)	7.0

These results indicate that the more favourable whisker distribution of variant B has resulted in a reduced notch wear.

Example 5

A ceramic slurry was manufactured in the same way and with the same composition as in the case of example 1 with the addition of polyvinylalcohol and glycerol to the slurry. The slurry was divided into two parts. One part was dried and granulated by conventional spray-drying technique. The other part was sprayed into a vessel containing liquid nitrogen and afterwards freeze dried at a temperature of about -20°C.

Both powders were manufactured in a B-SNGN120416 geometry by tool pressing. The compacted bodies were treated in a combined debinding and presintering cycle in a graphite furnace and surrounded by a covering BN-layer and on top of this a covering mullite layer and hot isostatic pressed according to example 3. The microstructure of the bodies made from freeze granulated powder showed an obvious more homogeneous distribution of SiC-whiskers compared to the bodies made from spray-dried powder.

Example 6

The bodies from the preceding example were ground into inserts with the style SNGN 120408 T02520 and tested in a turning operation developed to test toughness. The feed was continuously increased during the turning and the results were evaluated as feed at fracture (mean of 10 edges).

Result:	
Inserts A (priort art)	0.15 mm/rev
Inserts B (according to the invention)	0.20 mm/rev

These results show a significant difference between the inserts according to the invention and the prior art inserts. This indicates that the more favourable whisker distribution of inserts B has resulted in increased toughness.

Claims

1. Ceramic body comprising 2-50 volume-% whiskers and/or platelets and/or submicron particles in a ceramic matrix manufactured by conventional powder metallurgical methods, i.e., dispersion in a suitable liquid, granulation, compaction and sintering **characterized** in that the structure and composition is homogeneous, essentially free from granule borders and with an isotropic distribution of whiskers/platelets.

2. Body according to the preceding claim **characterized** in that said body is compacted by uniaxial compaction and the orientation of the whiskers/platelets is essentially two-dimensional.

3. Body according to any of the previous claims **characterized** in that said ceramic matrix is based on ceramic oxides, preferably Al_2O_3, or ceramic nitrides, preferably Si_3N_4.

4. Body according to claim 3 **characterized** in that said ceramic matrix further contains hard carbides and/or nitrides and/or borides and/or binder metal.

5. Body according to claim 3 or 4 **characterized** in that said matrix in addition contains <20 % by volume ZrO_2

6. Body according to any of the preceding claims **characterized** in that said whiskers consist of carbides, nitrides and/or borides of Si, Ti, Zr, Hf, Ta and/or Nb or solid solutions thereof.

7. Body according to the preceding claims 2 - 6 **characterized** in that said whiskers comprise SiC and that the degree of orientation (texture) of said whiskers determined by X-ray diffraction, T, T>3 preferably >4, most preferably >5, T being defined as (provided that the SiC-phase is present as >95% β-SiC-whiskers):

$$T = [(SiC_1/SiC_2)_p/(SiC_1/SiC_2)_c]^{0.5}$$

where SiC_1 = the intensity from the $\{10\bar{1}0\}$-peak of the hexagonal α-SiC

SiC_2 = the sum of the intensity from the (111)-peak of the cubic β-SiC and {0002} peak of the hexagonal α-SiC

p is from a plane perpendicular to the direction of the compaction

c is from a plane parallel to the direction of the compaction.

8. Body according to any of the preceding claims **characterized** in that said body is a cutting tool with complex geometry.

9. Granulated ceramic powder comprising 2-50 volume% whiskers and/or platelets and/or submicron particles manufactured by conventional powder metallurgical methods, i.e., dispersion in a suitable liquid, granulation **characterized** in that said powder comprises spherical granules the diameter of which is in the range of 0.01-1.0 mm, preferably 0.05-0.50 mm said granules having a uniform distribution of said whiskers and/or platelets.

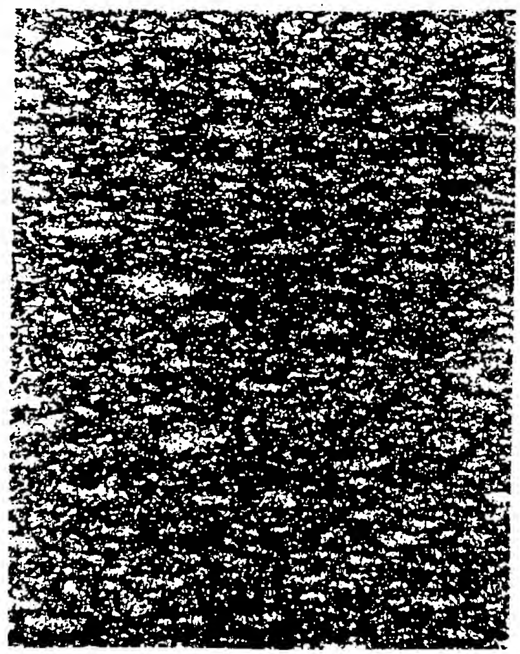

Fig. 1

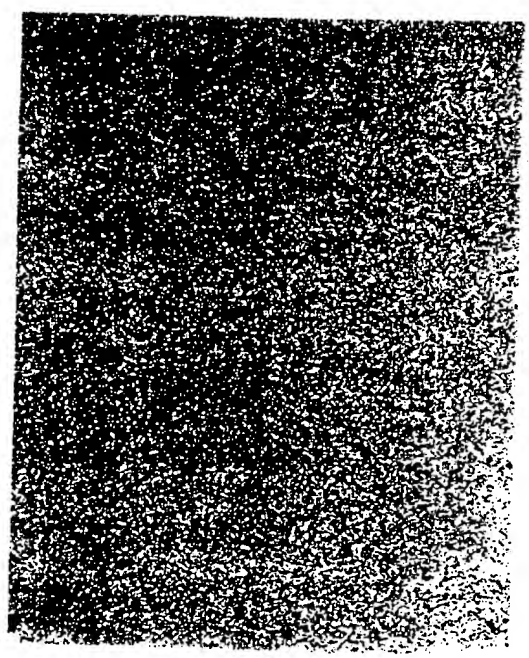

Fig. 2

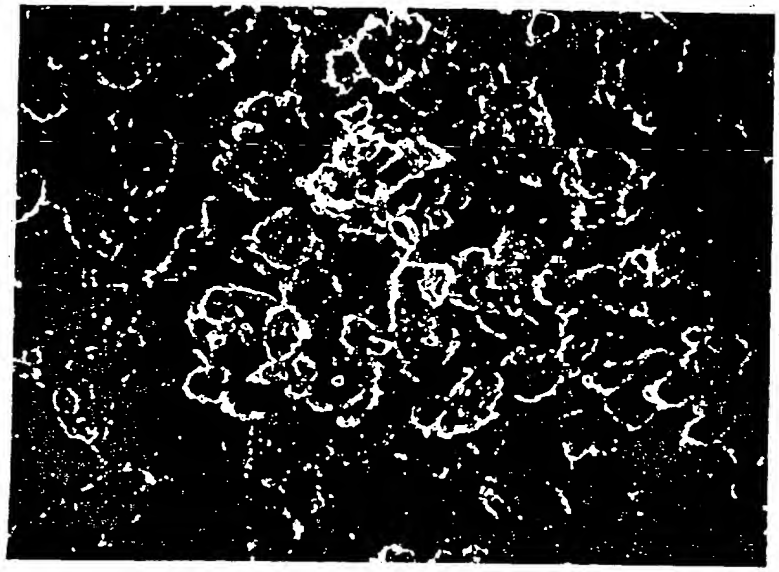

Fig. 3

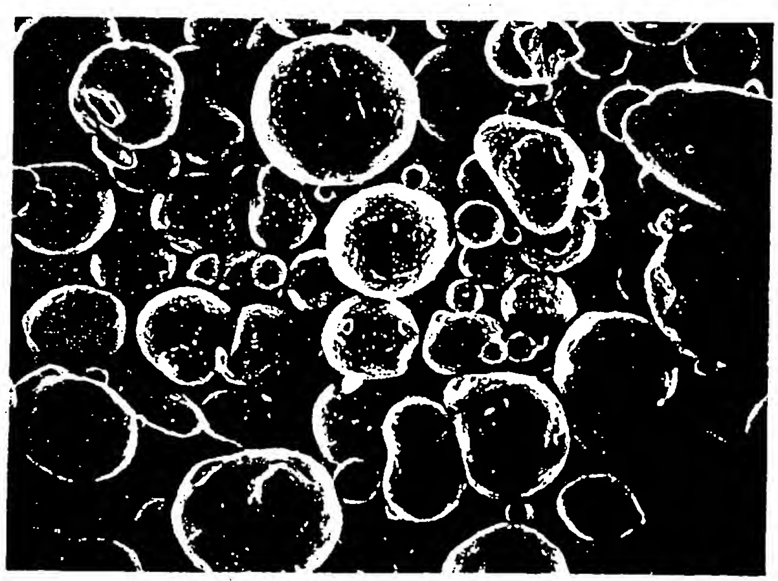

Fig. 4

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 85 0149

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,D	US-A-4 543 345 (G.C. WEI) * column 5, line 16 - line 21; claims 1,2,10; example 1 *	1-3,6-8	C04B35/80 C04B35/00 C04B35/58 C04B35/10
X	EP-A-0 414 910 (KABUSHIKI KAISHA KOBE SEIKO SHO) * page 3, line 22 - line 27; claims 1,3,5 *	1-3,6-8	
X,P,D	EP-A-0 506 640 (SANDVIK AKTIEBOLAG) * the whole document *	1,3-6,8,9	
X	WO-A-8 807 902 (CERAMICS SYSTEMS CORP.) * page 4, line 17 - page 5, line 8; claims 1,9 *	1,3-6,8,9	
X	WO-A-8 904 735 (CERAMICS PROCESS SYSTEMS CORP.) * page 11, line 29 - page 12, line 21 * * page 13, line 12 - line 17; claims 1,3,11-13,17 *	1,3-6,8,9	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 526 734 (R. ENOMOTO) * column 5, line 65 - column 6, line 18; claim 1; example 1 *	1-9	C04B
A	P.M.B. WALKER 'Chambers Science and Technology Dictionary' , CHAMBERS , CAMBRIDGE 1988 * page 434 * * page 484 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 OCTOBER 1993	LUETHE H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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